(19) World Intellectual Property Organization International Bureau



(43) International Publication Date 9 August 2001 (09.08.2001)

PCT

(10) International Publication Number WO 01/57099 A1

- (51) International Patent Classification7: C08F 10/00, 4/651, 4/654
- (21) International Application Number: PCT/EP01/00828
- (22) International Filing Date: 25 January 2001 (25.01.2001)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 00200342.4

2 February 2000 (02.02.2000) EF

- (71) Applicant (for all designated States except US): BASELL TECHNOLOGY COMPANY B.V. [NL/NL]; Hoeksteen 66, NL-2132 MS Hoofddorp (NL).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): MORINI, Giampiero [IT/IT]; Via Giotto, 36, I-35100 Padova (IT). BALBONTIN, Giulio [IT/IT]; Via Ugo Bassi 17/A, I-44100 Ferrara (IT). KLUSENER, Peter, A., A. [NL/NL]; Leideseweg 70, NL-3531 BE Utrecht (NL).
- (74) Agents: COLUCCI, Giuseppe; Basell Poliolefine Italia S.p.A., Intellectual Property, P. le G. Donegani, 12, I-44100 Ferrara et al. (IT).

- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COMPONENTS AND CATALYSTS FOR THE POLYMERIZATION OF OLEFINS

"COMPONENTS AND CATALYSTS FOR THE POLYMERIZATION OF OLEFINS"

The present invention relates to catalyst components for the polymerization of olefins, to the catalysts obtained therefrom and to the use of said catalysts in the polymerization of olefins CH₂=CHR in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms. In particular the present invention relates to catalyst components, suitable for the stereospecific polymerization of olefins, comprising Ti, Mg, halogen and an electron donor compound selected from esters of substituted succinic acids (substituted succinates). Said catalyst components when used in the polymerization of olefins, and in particular of propylene, are capable to give polymers in high yields and with high isotactic index expressed in terms of high xylene insolubility.

The chemical class of succinates is known in the art. However, the specific succinates of the present invention have never been used as internal electron donors in catalysts for the polymerization of olefins.

EP-A-86473 mentions the use of unsubstituted succinates as internal donors in catalyst components for the polymerization of olefins. The use of diisobutyl succinate and di-n-butyl succinate is also exemplified. The results obtained in terms of isotactic index and yields are however poor.

The use of polycarboxylic acid esters, including succinates, as internal donors in catalyst components for the polymerization of olefins, is also generically disclosed in EP 125911. Diethyl methylsuccinate and diallyl ethylsuccinate are mentioned in the description although they are not exemplified. Furthermore, EP263718 mentions, but does not exemplify, the use of diethyl methylsuccinate and di-n-butyl ethylsuccinate as internal donors. In order to check the performances of these succinates according to the teaching of the art the applicant has carried out some polymerization tests employing catalyst components containing diethyl methylsuccinate and diethyl ethylsuccinate, respectively, as internal donors. As shown in the experimental section, the so obtained catalysts gave an unsatisfactory activity/stereospecificity balance very similar to that obtained with catalysts containing unsubstituted succinates.

It has been therefore very surprising to discover that the specific substitution in the succinates of the invention generates compounds that, when used as internal donors, give catalyst components having improved activity and stereospecificity. It is therefore an object of the present invention to provide a solid catalyst component for the polymerization of olefins CH₂=CHR in which R is hydrogen or a hydrocarbon radical with 1-12 carbon atoms, comprising Mg, Ti, halogen and an electron donor selected from succinates of formula (I):

1

wherein the radicals R₁ and R₂, equal to or different from each other, are a C₁-C₂₀ linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms and the radical R₃ is a linear alkyl group having at least four carbon atoms optionally containing heteroatoms.

 R_1 and R_2 are preferably C_1 - C_8 alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl groups. Particularly preferred are the compounds in which R_1 and R_2 are selected from primary alkyls and in

$$\begin{array}{c|c}
R_3 & || \\
H \searrow C & O \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & | \\
 & |$$

particular branched primary alkyls. Examples of suitable R₁ and R₂ groups are methyl, ethyl, n-propyl, n-butyl, isobutyl, neopentyl, 2-ethylhexyl. Particularly preferred are ethyl, isobutyl, and neopentyl.

One of the preferred groups of compounds described by the formula (I) is that in which R_3 is a linear alkyl having from 4 to 20 carbon atoms. Particularly preferred are the compounds in which R_3 is a linear alkyl group having from 4 to 15 carbon atoms.

Specific examples of suitable monosubstituted succinate compounds are dimethyl n-butylsuccinate, dimethyl n-pentylsuccinate, dimethyl n-hexylsuccinate, dimethyl n-heptylsuccinate, dimethyl n-nonylsuccinate, dimethyl n-decylsuccinate, dimethyl n-dodecylsuccinate, dimethyl n-undecylsuccinate, diethyl n-pentylsuccinate, diethyl n-butylsuccinate, diethyl n-pentylsuccinate, diethyl n-hexylsuccinate, diethyl n-nonylsuccinate, diethyl n-nonylsuccinate, diethyl n-decylsuccinate, diethyl n-dodecylsuccinate, diethyl n-butylsuccinate, diethyl n-pentylsuccinate, diethyl n-hexylsuccinate, diisobutyl n-pentylsuccinate, diisobutyl n-nonylsuccinate, diisobutyl n-nonylsuccinate, diisobutyl n-decylsuccinate, diisobutyl n-decylsuccinate, diisobutyl n-nonylsuccinate, diisobutyl n-decylsuccinate, diisobutyl n-nonylsuccinate, diisobutyl n-decylsuccinate, diisobutyl n-nonylsuccinate, diisobutyl n-decylsuccinate, diisobutyl n-nonylsuccinate, diisobutyl n-nonylsuccinate, diisobutyl n-nonylsuccinate, diisobutyl n-decylsuccinate, diisobutyl n-nonylsuccinate, diisobutyl n

octylsuccinate, dineopentyl n-nonylsuccinate, dineopentyl n-decylsuccinate, dineopentyl n-undecylsuccinate, dineopentyl n-dodecylsuccinate, dineopentyl tetradecylsuccinate, di-n-butyl n-butylsuccinate, di-n-butyl n-pentylsuccinate, di-n-butyl n-hexylsuccinate, di-n-butyl n-heptylsuccinate, di-n-butyl n-nonylsuccinate, di-n-butyl n-decylsuccinate, di-n-butyl n-dodecylsuccinate, di-n-butyl n-dodecylsuccinate, di-n-butyl n-hexylsuccinate, methyl ethyl n-butylsuccinate, methyl ethyl n-pentylsuccinate, methyl ethyl n-nonylsuccinate, methyl ethyl n-nonylsuccinate, methyl ethyl n-dodecylsuccinate, methyl ethyl n-dodecylsuccinate, methyl ethyl n-hexylsuccinate, isobutyl ethyl n-butylsuccinate, isobutyl ethyl n-hexylsuccinate, isobutyl ethyl n-hexylsuccinate, isobutyl ethyl n-hexylsuccinate, isobutyl ethyl n-nonylsuccinate, isobutyl ethyl n-decylsuccinate, isobutyl ethyl n-nonylsuccinate, isobutyl ethyl n-dodecylsuccinate, isobutyl ethyl n-undecylsuccinate, isobutyl eth

It is easily derivable for the ones skilled in the art that all the above mentioned compounds can be used either in form of pure isomers or in the form of mixtures of enantiomers, or mixture of regioisomers and enantiomers. When a pure isomer is to be used it is normally isolated using the common techniques known in the art.

As explained above, the catalyst components of the invention comprise, in addition to the above electron donors, Ti, Mg and halogen. In particular, the catalyst components comprise a titanium compound, having at least a Ti-halogen bond and the above mentioned electron donor compound supported on a Mg halide. According to the present invention with the term supported on a Mg halide are meant the Ti compound and the electron donor compounds which are not extractable to an extent higher than 50% when the extraction is carried out with heptane at 80°C in 2 hours. The magnesium halide is preferably MgCl₂ in active form which is widely known from the patent literature as a support for Ziegler-Natta catalysts. Patents USP 4,298,718 and USP 4,495,338 were the first to describe the use of these compounds in Ziegler-Natta catalysis. It is known from these patents that the magnesium dihalides in active form used as support or co-support in components of catalysts for the polymerization of olefins are characterized by X-ray spectra in which the most intense diffraction line that appears in the spectrum of the non-active halide is diminished in intensity and is replaced by a halo whose maximum intensity is displaced towards lower angles relative to that of the more intense line.

The preferred titanium compounds used in the catalyst component of the present invention are

TiCl₄ and TiCl₃; furthermore, also Ti-haloalcoholates of formula Ti(OR)_{n-y} X_y , where n is the valence of titanium and y is a number between 1 and n, can be used.

The preparation of the solid catalyst component can be carried out according to several methods. According to one of these methods, the magnesium dichloride in an anhydrous state and the succinate of formula (I) are milled together under conditions in which activation of the magnesium dichloride occurs. The so obtained product can be treated one or more times with an excess of TiCl₄ at a temperature between 80 and 135°C. This treatment is followed by washings with hydrocarbon solvents until chloride ions disappeared. According to a further method, the product obtained by co-milling the magnesium chloride in an anhydrous state, the titanium compound and the substituted succinate is treated with halogenated hydrocarbons such as 1,2-dichloroethane, chlorobenzene, dichloromethane etc. The treatment is carried out for a time between 1 and 4 hours and at a temperature ranging from 40°C to the boiling point of the halogenated hydrocarbon. The product obtained is then generally washed with inert hydrocarbon solvents such as hexane.

According to another method, magnesium dichloride is preactivated according to well known methods and then treated with an excess of TiCl₄ at a temperature of about 80 to 135°C which contains, in solution, a succinate of formula (I). The treatment with TiCl₄ is repeated and the solid is washed with hexane in order to eliminate any non-reacted TiCl₄.

A further method comprises the reaction between magnesium alcoholates or chloroalcoholates (in particular chloroalcoholates prepared according to U.S. 4,220,554) and an excess of TiCl₄ comprising the succinate of formula (I) in solution at a temperature of about 80 to 120°C.

According to a preferred method, the solid catalyst component can be prepared by reacting a titanium compound of formula Ti(OR)_{n-y}X_y, where n is the valence of titanium and y is a number between 1 and n, preferably TiCl₄, with a magnesium chloride deriving from an adduct of formula MgCl₂•pROH, where p is a number between 0.1 and 6, preferably from 2 to 3.5, and R is a hydrocarbon radical having 1-18 carbon atoms. The adduct can be suitably prepared in spherical form by mixing alcohol and magnesium chloride in the presence of an inert hydrocarbon immiscible with the adduct, operating under stirring conditions at the melting temperature of the adduct (100-130°C). Then, the emulsion is quickly quenched, thereby causing the solidification of the adduct in form of spherical particles. Examples of spherical adducts prepared according to this procedure are described in USP 4,399,054 and USP 4,469,648. The so obtained adduct can be directly reacted with the Ti compound or it can be previously subjected to

thermal controlled dealcoholation (80-130°C) so as to obtain an adduct in which the number of moles of alcohol is generally lower than 3 preferably between 0.1 and 2.5. The reaction with the Ti compound can be carried out by suspending the adduct (dealcoholated or as such) in cold TiCl₄ (generally 0°C); the mixture is heated up to 80-130°C and kept at this temperature for 0.5-2 hours. The treatment with TiCl₄ can be carried out one or more times. The succinate of formula (I) can be added during the treatment with TiCl₄. The treatment with the electron donor compound can be repeated one or more times.

The preparation of catalyst components in spherical form is described for example in European Patent Applications EP-A-395083, EP-A-553805, EP-A-553806, EPA-601525 and WO98/44001.

The solid catalyst components obtained according to the above method show a surface area (by B.E.T. method) generally between 20 and 500 m²/g and preferably between 50 and 400 m²/g, and a total porosity (by B.E.T. method) higher than 0.2 cm³/g preferably between 0.2 and 0.6 cm³/g. The porosity (Hg method) due to pores with radius up to 10.000Å generally ranges from 0.3 to 1.5 cm³/g, preferably from 0.45 to 1 cm³/g.

A further method to prepare the solid catalyst component of the invention comprises halogenating magnesium dihydrocarbyloxide compounds, such as magnesium dialkoxide or diaryloxide, with solution of TiCl₄ in aromatic hydrocarbon (such as toluene, xylene etc.) at temperatures between 80 and 130°C. The treatment with TiCl₄ in aromatic hydrocarbon solution can be repeated one or more times, and the substituted succinate is added during one or more of these treatments.

In any of these preparation methods the desired succinate of formula (I) can be added as such or, in an alternative way, it can be obtained *in situ* by using an appropriate precursor capable to be transformed in the desired electron donor compound by means, for example, of known chemical reactions such as esterification, transesterification, etc. Generally, the succinate of formula (I) is used in molar ratio with respect to the MgCl₂ ranging from 0.01 to 1 and preferably from 0.05 to 0.5.

The solid catalyst components according to the present invention are converted into catalysts for the polymerization of olefins by reacting them with organoaluminum compounds according to known methods.

In particular, it is an object of the present invention a catalyst for the polymerization of olefins CH_2 =CHR, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising

the product of the reaction between:

(a) a solid catalyst component comprising a Mg, Ti and halogen and an electron donor selected from succinates of formula (I);

- (b) an alkylaluminum compound and, optionally,
- (c) one or more electron-donor compounds (external donor).

The alkyl-Al compound (b) is preferably selected from the trialkyl aluminum compounds such as for example triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum. It is also possible to use mixtures of trialkylaluminum compounds with alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides, such as AlEt₂Cl and Al₂Et₃Cl₃.

The external donor (c) can be of the same type or it can be different from the succinate of formula (I). Suitable external electron-donor compounds include silicon compounds, ethers, esters such as phthalates, benzoates, succinates also having a different structure from those of formula (I), amines, heterocyclic compounds and particularly 2,2,6,6-tetramethylpiperidine, ketones and the 1,3-diethers of the general formula (II):

$$\begin{array}{ccc}
R^{II} & R^{I} \\
R^{III} & OR^{VIII} \\
R^{IV} & OR^{VII}
\end{array}$$
(II)

wherein R^I , R^{II} , R^{III} , R^{IV} , R^V and R^{VI} equal or different to each other, are hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and R^{VII} and R^{VIII} , equal or different from each other, have the same meaning of R^I-R^{VI} except that they cannot be hydrogen; one or more of the R^I-R^{VIII} groups can be linked to form a cycle. Particularly preferred are the 1,3-diethers in which R^{VIII} and R^{VIII} are selected from C_1-C_4 alkyl radicals.

Another class of preferred external donor compounds is that of silicon compounds of formula $R_a{}^5R_b{}^6Si(OR^7)_c$, where a and b are integers from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^5 , R^6 , and R^7 , are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms. Particularly preferred are the silicon compounds in which a is 1, b is 1, c is 2, at least one of R^5 and R^6 is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms optionally containing heteroatoms and R^7 is a C_1 - C_{10} alkyl group,

Examples of such preferred silicon compounds particular methyl. in methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, (2-ethylpiperidinyl)t-butyldimethoxysilane, dicyclopentyldimethoxysilane, (2-(3,3,3-trifluoro-n-propyl)(2ethylpiperidinyl)thexyldimethoxysilane, ethylpiperidinyl)dimethoxysilane, methyl(3,3,3-trifluoro-n-propyl)dimethoxysilane. Moreover, are also preferred the silicon compounds in which a is 0, c is 3, R⁶ is a branched alkyl or cycloalkyl group, optionally containing heteroatoms, and R7 is methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, t-butyltrimethoxysilane and thexyltrimethoxysilane.

The electron donor compound (c) is used in such an amount to give a molar ratio between the organoaluminum compound and said electron donor compound (c) ranging from 0.1 to 500, preferably from 1 to 300 and more preferably from 3 to 100. As previously indicated, when used in the (co)polymerization of olefins, and in particular of propylene, the catalysts of the invention allow to obtain, with high yields, polymers having a high isotactic index (expressed by high xylene insolubility X.I.), thus showing an excellent balance of properties. This is particularly surprising in view of the fact that, as it can be seen from the comparative examples here below reported, the use as internal electron donors of unsubstituted succinate compounds gives worse results in term of yields and/or xylene insolubility.

As mentioned above, the succinates of the present invention can also be useful as external donors in catalysts for the polymerization of olefins. Accordingly, another object of the present invention is a catalyst for the polymerization of olefins CH₂=CHR, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product of the reaction between:

- (i) a solid catalyst component comprising a Mg, Ti and halogen and optionally containing an electron donor compound;
- (ii) an alkylaluminum compound and,
- (iii) one or more electron-donor compounds (external donor) selected from succinates of formula (I).

The electron donor compound present on the catalyst component (i) can be selected from the same classes described for the electron donor (c). Preferably, it is selected from esters like phthalates and the 1,3-diethers of formula (II) disclosed above.

According to what has been mentioned above it constitutes a particular object of the present invention a process for the (co)polymerization of olefins CH₂=CHR, in which R is hydrogen or a

hydrocarbyl radical with 1-12 carbon atoms, carried out in the presence of a catalyst comprising the product of the reaction between:

- (a) a solid catalyst component comprising a Mg, Ti, halogen and an electron donor selected from succinates of formula (I);
- (b) an alkylaluminum compound and, optionally,
- (c) one or more electron-donor compounds (external donor).

Said polymerization process can be carried out according to known techniques for example slurry polymerization using as diluent an inert hydrocarbon solvent, or bulk polymerization using the liquid monomer (for example propylene) as a reaction medium. Moreover, it is possible carrying out the polymerization process in gas-phase operating in one or more fluidized or mechanically agitated bed reactors.

The polymerization is generally carried out at temperatures ranging from 20 to 120°C, preferably from 40 to 80°C. When the polymerization is carried out in gas-phase the operating pressure is generally between 0.5 and 10 MPa, preferably between 1 and 5 MPa. In the bulk polymerization the operating pressure is generally between 1 and 6 MPa preferably between 1.5 and 4 MPa. Hydrogen or other compounds capable to act as chain transfer agents can be used to control the molecular weight of the polymer.

The following examples are given in order to better illustrate the invention without limiting it.

CHARACTERIZATIONS

Preparation of succinates

Succinates have been prepared according to known methods described in the literature, (for example by alkylation of dialkyl succinates: N.R. Long and M.W. Rathke, Synthetic Commun. 11, 687, 1981; W.G. Kofron and L.G. Wideman, J. Org. Chem. 37, 555, 1972; by esterification of alkylsuccinates: "Vogel's textbook of practical organic chemistry", 5th Edition (1989), pages 695 - 707; by coupling of acids or alkyl monoesters: J.L. Belletire, E.G. Spletzer and A.R. Pinhas, Tetrahedron Lett. 25, 5969, 1984; N. Petragnani, and M. Yonahiro, Synthesis, 710, 1980; by addition to dialkyl maleates of dialkyl fumarates: T. Ibuka, T. Aoyagi, K. Kitada, F. Yoneda and Y. Yamamoto, J. Organomet. Chem., 287, C18, 1985; E.B. Nielsen, J. Munch-Petersen, P.M. Jorgensen and S. Refn, Acta Chem. Scand., 13, 1959; V.K. Andersen and J. Munch-Petersen, Acta Chem. Scand., 16, 947, 1962; J. Munch-Petersen and V.K. Andersen, Acta Chem. Scand., 15, 271, 1961).

Propvlene polymerization: general procedure

In a 4 liter autoclave, purged with nitrogen flow at 70°C for one hour, 75 mL of anhydrous hexane containing 800 mg of AlEt₃, 79.8 mg of dicyclopentyldimethoxysilane and 10 mg of solid catalyst component were introduced in propylene flow at 30°C. The autoclave was closed. 1.5 NL of hydrogen were added and then, under stirring, 1.2 Kg of liquid propylene were fed. The temperature was risen to 70°C in five minutes and the polymerization was carried out at this temperature for two hours. The non-reacted propylene was removed, the polymer was collected, dried at 70°C under vacuum for three hours, weighed, and fractionated with o-xylene to determine the amount of the xylene insoluble (X.I.) fraction at 25°C.

Determination of X.I.

2.5 g of polymer were dissolved in 250 mL of o-xylene under stirring at 135°C for 30 minutes, then the solution was cooled to 25°C and after 30 minutes the insoluble polymer was filtered. The resulting solution was evaporated in nitrogen flow and the residue was dried and weighed to determine the percentage of soluble polymer and then, by difference the xylene insoluble fraction (%).

EXAMPLES

Examples 1-3 and Comparative Examples 4-5

Preparation of solid catalyst components.

Into a 500 mL four-necked round-bottomed flask, purged with nitrogen, 250 mL of TiCl₄ were introduced at 0°C. While stirring, 10.0 g of microspheroidal MgCl₂*2.8C₂H₅OH (prepared according to the method described in ex.2 of USP 4,399,054 but operating at 3,000 rpm instead of 10,000 rpm) and 7.4 mMoles of succinate were added. The temperature was raised to 100°C and maintained for 120 min. Then, the stirring was discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off.

250 mL of fresh TiCl₄ were added. The mixture was reacted at 120°C for 60 min and, then, the supernatant liquid was siphoned off. The solid was washed six times with anhydrous hexane (6 x 100 mL) at 60°C. Finally, the solid was dried under vacuum and analyzed. The type and amount of succinate (wt %) and the amount of Ti (wt %) contained in the solid catalyst component are reported in Table 1. Polymerization results are reported in Table 2.

Table 1

Ex.	Succinate		Ti	
		Wt %	Wt %	
1	Diethyl n-butylsuccinate	7.1	3.0	
2	Diethyl n-hexylsuccinate	11.2	3.3	
3	Diethyl n-decylsuccinate	17.1	3.4	
Comp. 4	Diethyl methylsuccinate	10.9	3.4	
Comp. 5	Diethyl ethylsuccinate	10.1	2.7	

Table 2

Example	Yield	X.I.
n.	KgPP/gCat	Wt %
1	22	97.5
2	21	97.2
3	30	97.0
Comp.4	11	95.8
Comp.5	14	96.5

CLAIMS

1. A solid catalyst component for the polymerization of olefins CH₂=CHR, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising Mg, Ti, halogen and an electron donor selected from succinates of formula (I):

wherein the radicals R_1 and R_2 , equal to or different from each other, are C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl groups, optionally containing heteroatoms and the radical R_3 is a linear alkyl group having at least four carbon atoms optionally containing heteroatoms.

- Catalyst component according to claim 1 in which the electron donor compound of formula
 (I) is selected from those in which R₁ and R₂ are C₁-C₈ alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl groups.
- 3. Catalyst components according to claim 2 in R₁ and R₂ are selected from primary alkyls.
- 4. Catalyst components according to claim 3 in which R₁ and R₂ are selected from ethyl, isobutyl and neopentyl.
- 5. Catalyst component according to any of the preceding claims in which the electron donor compound of formula (I) is selected from those in which R₃ is a linear alkyl having from 4 to 20 carbon atoms.
- 6. Catalyst components according to claim 5 in which R₃ is a linear alkyl group having from 4 to 15 carbon atoms.
- 7. Catalyst components according to claim 1 in which the succinates are selected from the group consisting of diethyl n-butylsuccinate, diethyl n-pentylsuccinate, diethyl n-hexylsuccinate, diethyl n-heptylsuccinate, diethyl n-octylsuccinate, diethyl n-nonylsuccinate, diethyl n-decylsuccinate, diethyl n-undecylsuccinate, diethyl n-decylsuccinate, diethyl n-butylsuccinate, diethyl tetradecylsuccinate, diisobutyl n-butylsuccinate,

diisobutyl n-pentylsuccinate, diisobutyl n-hexylsuccinate, diisobutyl n-heptylsuccinate, diisobutyl n-octylsuccinate, diisobutyl n-nonylsuccinate, diisobutyl n-decylsuccinate, diisobutyl n-dodecylsuccinate, diisobutyl tetradecylsuccinate, dineopentyl n-butylsuccinate, dineopentyl n-pentylsuccinate, dineopentyl n-hexylsuccinate, dineopentyl n-heptylsuccinate, dineopentyl n-octylsuccinate, dineopentyl n-nonylsuccinate, dineopentyl n-decylsuccinate, dineopentyl n-undecylsuccinate, dineopentyl n-dodecylsuccinate, dineopentyl tetradecylsuccinate

- 8. A solid catalyst component according to claim 1 comprising a titanium compound having at least a Ti-halogen bond and the succinate of formula (I) supported on a Mg halide in active form.
- 9. A solid catalyst component according to claim 8 in which the titanium compound is TiCl₄ or TiCl₃.
- 10. A catalyst for the polymerization of olefins CH₂=CHR, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product of the reaction between:
 - (a) the solid catalyst component of any of the claims 1-9;
 - (b) an alkylaluminum compound and, optionally,
 - (c) one or more electron-donor compounds (external donor).
- 11. Catalyst according to claim 10 in which the alkylaluminum compound (b) is a trialkyl aluminum compound.
- 12. Catalyst according to claim 11 in which the trialkyl aluminum compound is selected from the group consisting of triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum.
- 13. Catalyst according to claim 10 in which the external donor (c) is a silicon compound of formula. $R_a^5 R_b^6 Si(OR^7)_c$, where a and b are integers from 0 to 2, c is an integer from 1 to 4 and the sum (a+b+c) is 4; R^5 , R^6 and R^7 are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms.
- 14. Catalyst according to claim 13 in which a is 1, b is 1 and c is 2.
- 15. Catalyst according to claim 13 in which R⁵ and/or R⁶ are branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms optionally containing heteroatoms and R⁷ is a C₁-C₁₀ alkyl group, in particular methyl.
- 16. Catalyst according to claim 13 in which a is 0, c is 3 and R⁶ is a branched alkyl or cycloalkyl

- group and R⁷ is methyl.
- 17. Catalyst according to claim 13 in which the silicon compound is selected from the group consisting of methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, dicyclopentyldimethoxysilane, (2-ethylpiperidinyl)t-butyldimethoxysilane, (2-ethylpiperidinyl)thexyldimethoxysilane, (3,3,3-trifluoro-n-propyl)(2-ethylpiperidinyl)dimethoxysilane, methyl(3,3,3-trifluoro-n-propyl)dimethoxysilane.
- 18. Process for the (co)polymerization of olefins CH₂=CHR, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, carried out in the presence of any of the catalysts of claims 10-17.
- 19. Catalyst for the polymerization of olefins CH₂=CHR, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product of the reaction between:
 - a solid catalyst component comprising a Mg, Ti and halogen and optionally containing an electron donor compound;
 - an alkylaluminum compound and,
 - one or more electron-donor compounds (external donor) selected from succinates of formula (I).
- 20. Use of succinates of formula (I) as electron donors in catalyst for the polymerization of olefins.

INTERNATIONAL SEARCH REPORT

Ir. ational Application No PCT/EP 01/00828

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 CO8F10/00 CO8F CO8F4/651 C08F4/654 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) C08F Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, CHEM ABS Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Category ° Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. DATABASE WPI 1 - 20Α Section Ch. Week 198339 Derwent Publications Ltd., London, GB; Class A17, AN 1983-773196 XP002165744 & JP 58 138709 A (MITSUI PETROCHEM IND CO LTD), 17 August 1983 (1983-08-17) abstract Α DATABASE WPI 1 - 20Section Ch, Week 199033 Derwent Publications Ltd., London, GB; Class A17, AN 1990-249819 XP002165745 & JP 02 173105 A (TAIWAN SOKO KOGYO K), 4 July 1990 (1990-07-04) abstract -/--Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the *A* document defining the general state of the art which is not considered to be of particular relevance invention 'E' earlier document but published on or after the international *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another "Y" document of particular relevance; the claimed invention citation or other special reason (as specified) cannot be considered to involve an inventive step when the document is combined with one or more other such docu-*O* document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled other means document published prior to the international filing date but later than the priority date claimed *&* document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 23 April 2001 12/06/2001 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040. Tx. 31 651 epo nl. Fax: (+31-70) 340-3016 Parry, J

1

INTERNATIONAL SEARCH REPORT

II .iational Application No PCT/EP 01/00828

C.(Continu	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category °	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 522 930 A (ALBIZZATI ENRICO ET AL) 11 June 1985 (1985-06-11) column 9; examples 5,6	1-20
A	EP 0 267 794 A (NIPPON PETROCHEMICALS CO LTD) 18 May 1988 (1988-05-18) page 7, line 21 - line 34	1-20
Ρ,Χ	WO 00 63261 A (BALBONTIN GIULIO ;MORINI GIAMPIERO (IT); MONTELL TECHNOLOGY COMPAN) 26 October 2000 (2000-10-26) page 2 -page 6	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

h hational Application No PCT/EP 01/00828

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 58138709 A	17-08-1983	JP 1684786 C JP 3048210 B	31 - 07-1992 23 - 07-1991
JP 2173105 A	04-07-1990	JP 2005091 C JP 7033407 B	11-01-1996 12-04-1995
US 4522930 A	11-06-1985	IT 1190683 B AT 27286 T AU 561820 B AU 1128583 A BR 8300673 A CA 1211099 A DE 3371638 D EP 0086473 A ES 519706 D ES 8403142 A GR 77923 A IN 161721 A JP 8016124 B JP 58145707 A JP 2693707 B JP 6192316 A MX 163288 A PT 76225 A,B US 4904628 A	24-02-1988 15-06-1987 21-05-1987 18-08-1983 08-11-1983 09-09-1986 25-06-1987 24-08-1983 16-03-1984 01-06-1984 25-09-1984 23-01-1988 21-02-1996 30-08-1983 24-12-1997 12-07-1994 09-04-1992 01-03-1983 27-02-1990
EP 0267794 A	18-05-1988	JP 63122710 A DE 3785723 A DE 3785723 T	26-05-1988 09-06-1993 12-08-1993
WO 0063261 A	26-10-2000	AU 4548600 A BR 0006095 A EP 1088009 A NO 20006388 A	02-11-2000 20-03-2001 04-04-2001 29-01-2001